# Electronic Supplementary Information

## A self-assembled bisoxazoline/Pd composite microsphere as an excellent catalyst for Suzuki-Miyaura coupling reaction

Junke Wang [a,b,c], Yingxiao Zong [a,b], Xicun Wang*[,b], Yulai Hu[b], Guoren Yue[a] and Yi Pan[c]

[a.] *Key Laboratory of Hexi corridor resources utilization of Gansu Universities, College of Chemistry and Chemical Engineering, Hexi University, Zhangye 734000, China*

[b.] *Gansu Key Laboratory of Polymer Materials, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China*

[c.] *College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

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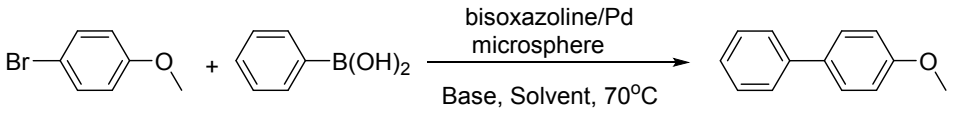
## 1. Materials and methods

Melting points were determined on a Perkin-Elmer differential scanning calorimeter and were uncorrected. The IR spectra were run on a Nicolete spectrometer (KBr). NMR spectra were recorded at 400 ($^{1}$H) and 100 ($^{13}$C) MHz, respectively, on a Varian Mercury plus-400 instrument using $CDCl_3$ as solvent and TMS as the internal standard. Scanning electron microscopy (SEM) was performed on a FEI Quanta 450 FEG FESEM instrument. High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). All the solvents used were strictly dried according to standard operation and stored on 4 Å molecular sieves. Flash chromatography columns were packed with 200-300 mesh silica gel.

All other chemicals (AR grade) were commercially available and used without further purification.

## 2.Optimization of the catalytic conditions

**Table 1** The effect of solvents and bases[a]




| Entry | Solvent | Base | Time( h) | Yield(%)[b] |
|---|---|---|---|---|
| 1 | $H_2O$ | $Na_2CO_3$ | 2 | 15 |
| 2 | $H_2O$ | $K_2CO_3$ | 2 | 29 |
| 3 | $H_2O$ | $NaHCO_3$ | 2 | 10 |
| 4 | $H_2O$ | NaOAc | 2 | 18 |
| 5 | $H_2O$ | TEA | 2 | 8 |
| 6 | $H_2O$:EtOH (2:1) | $K_2CO_3$ | 2 | 41 |
| 7 | $H_2O$:EtOH (1:1) | $K_2CO_3$ | 2 | 50 |
| 8 | $H_2O$:EtOH (1:2) | $K_2CO_3$ | 2 | 65 |
| 9 | EtOH | $K_2CO_3$ | 2 | 20 |
| 10 | Toluene | $K_2CO_3$ | 2 | 28 |
| 11 | DMF | $K_2CO_3$ | 2 | 5 |
| 12 | dioxane | $K_2CO_3$ | 2 | 7 |
| 13 | $H_2O$:PEG-400 (5:1) | $K_2CO_3$ | 2 | 85 |
| 14 | $H_2O$:PEG-400 (8:1) | $K_2CO_3$ | 2 | 84 |
| 15 | $H_2O$:PEG-400 (10:1) | $K_2CO_3$ | 2 | 84 |
| 16 | $H_2O$:PEG-400 (10:1) | $K_2CO_3$ | 3 | 93 |
| 17 | $H_2O$:PEG-400 (10:1) | $K_2CO_3$ | 4 | 98 |

[a] Reaction conditions: bisoxazoline/Pd microsphere containing 0.1mol% Pd, 1 mmol of *p*-bromoanisole, 1 mmol of phenylboronic acid, 2 mmol of base, 5 ml of solvent , 70 °C in air.
[b] Isolated yield.

## 3. Preparation and analytical data of catalyst C

**Synthesis of bisacylthiourea B**

To a solution of 4,4'-Oxybisbenzoyl chloride **A** (2 mmol) in $CH_2Cl_2$ (10 mL) was added ammonium thiocyanate (2.6 mmol) and PEG-400 (0.2 mmol). The mixture was then stirred at room temperature for 60 min and cooled to 0˚C, and the solution of 2-aminoethanol (1.8 mmol) in $CH_2Cl_2$ (2 mL) was added. The mixture was continuously stirred for 60 min. After the completion of the reaction, the solvent was removed by distillation, and water (10 mL) was added to obtain a white solid. The analytical sample was produced by flash chromatography(acetone and petroleum ether) to give a white solid **B**. Yield: 85%. Spectral data: IR (KBr) ($cm^{-1}$): ν 3337, 3225, 2944, 1670, 1531. $^1$H NMR (400 MHz, DMSO) δ 11.35 (s, 2H), 11.05 (s, 2H), 8.02 (d, *J* = 8.8 Hz, 4H), 7.17 (d, *J* = 8.8 Hz, 4H), 4.98 (s, 2H), 3.83-3.44 (m, 8H). $^{13}$C NMR (100 MHz, DMSO) δ 180.71 (s), 167.65 (s), 159.87 (s), 131.68 (s), 128.22 (s), 118.95 (s), 58.75 (s), 47.97 (s), 40.38 (s), 40.17 (s), 39.96 (s), 39.75 (s), 39.54 (s). HR-MS: m/z calcd for $C_{20}H_{21}N_2O_5S_2$ $[M+H]^+$: 433.0892; found: 433.0889.

**Synthesis of bisoxazoline C**

To a solution of compound **B** (1 mmol) in DMF (5 mL) was added dicyclohexylcarbodiimide (DCC) (1 mmol ) and TEA(1 mmol ). The mixture was stirred for 2 h at 80$^o$C, and cooled to room temperature. After the addition of water (5 mL), the white solid was obtained by the filtration. This solid was added into $CH_3CN$ (5 mL) to be dissolved, followed by the filtration and concentration to afford the target compound **C**. Yield: 98%. Spectral data: IR (KBr) ($cm^{-1}$): ν 3310, 2921, 1638, 1548. $^1$H NMR (400 MHz, DMSO) δ 9.61 (s, 2H), 8.28 – 7.99 (m, 4H), 7.20 – 6.98 (m, 4H), 4.47 (t, J = 8.6 Hz, 4H), 3.78 (t, J = 8.6 Hz, 4H). $^{13}$C NMR (100 MHz, DMSO) δ 180.71, 167.65, 159.87, 131.68, 128.22, 118.95, 58.75, 47.97, 40.59, 40.38, 40.17, 39.96, 39.75, 39.54, 39.33. HR-MS: m/z calcd for $C_{20}H_{19}N_4O_5$ $[M+H]^+$: 395.1355; found: 395.1395.

**Synthesis of catalyst D**

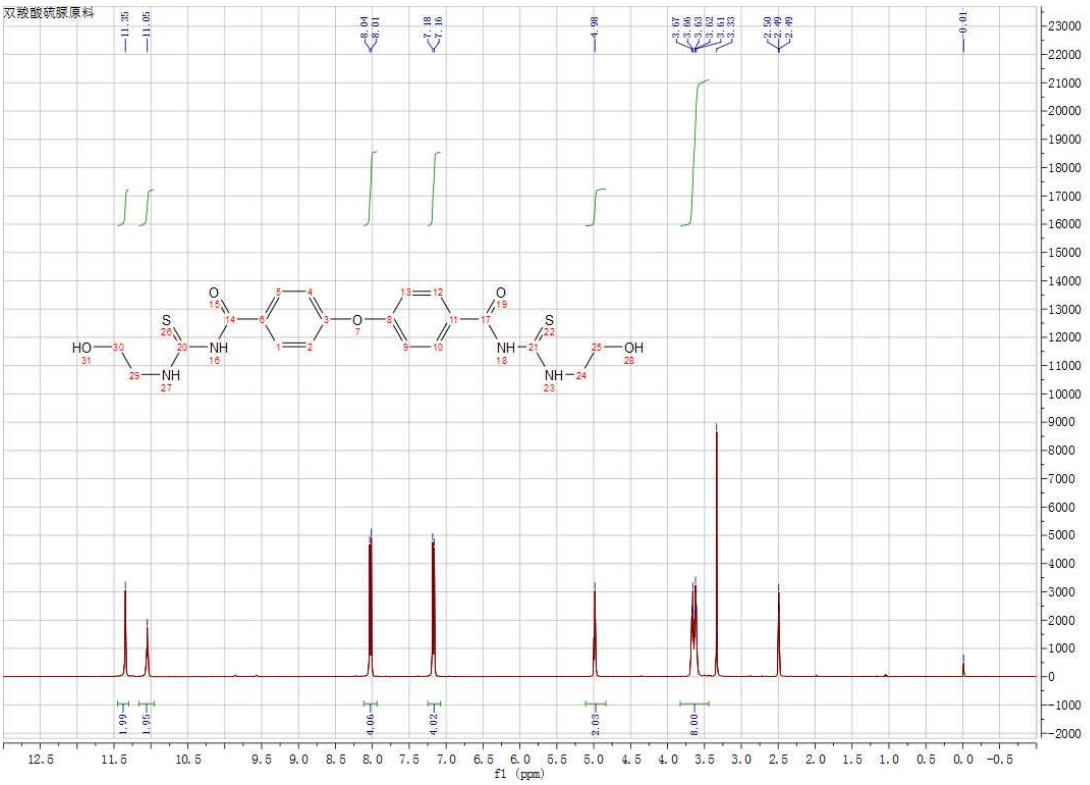
To the solution of $Pd(AcO)_2$ (2 mmol) in $CH_3CN$ (5 mL) was added dropwise into the obtained compound C (1.36 g, 6 mmol) in $CH_3CN$ (2 mL), followed by the stiring for 10 h. On completion, the filtration was conducted to a yellow solid. Washing with commercial anhydrous $CH_3CN$ (3 × 5 mL) and drying at 50 °C overnight gave bisoxazoline/Pd microsphere as a pale yellow powder( compound D). IR (KBr) ($cm^{-1}$): ν 3443, 2907, 1592. The Pd content of the bisoxazoline/Pd microsphere catalyst is 20.01 wt% (1.8 mmol/g) measured by atomic absorption spectroscopy (AAS).

**4. General Experimental Procedures for Suzuki-Miyaura Couplings**

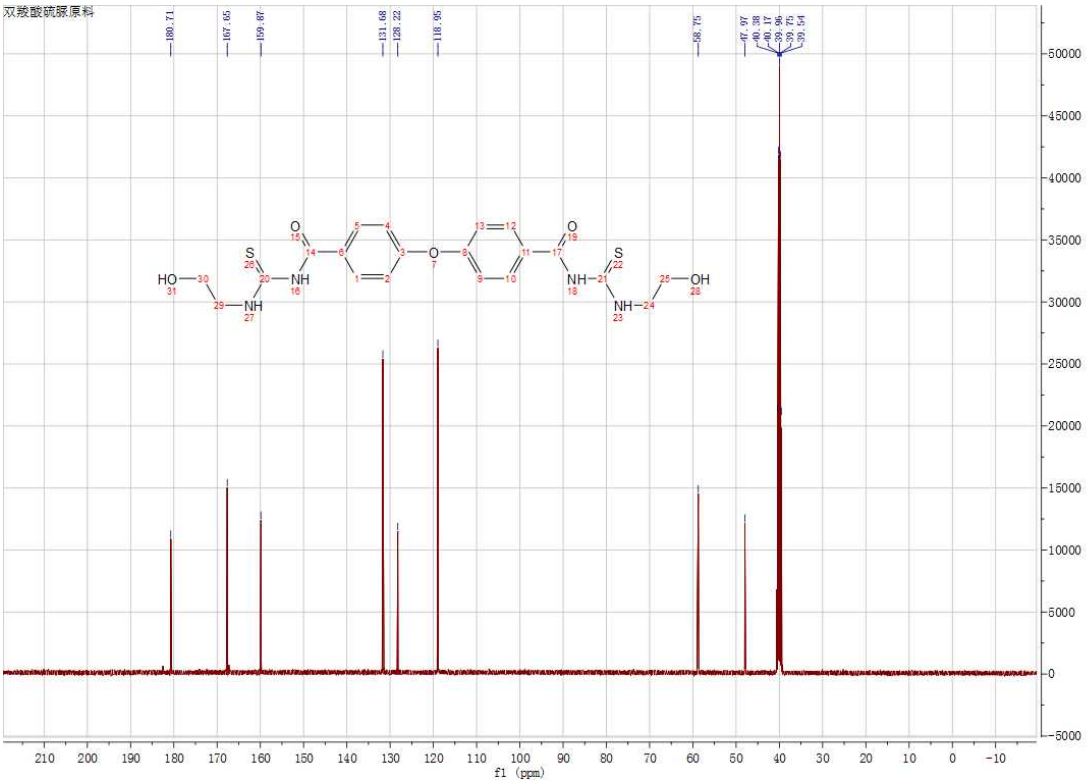
In a typical experiment, the bisoxazoline/Pd microsphere catalyst (0.005 mmol of Pd) was added to a mixture of aryl halide (1.2 mmol), arylboronic acid (1.0 mmol), PEG-400(0.1 mmol) and $K_2CO_3$ (2.0 mmol) in water (5.0 mL), and the reaction mixture was stirred at reflux. After the reaction was monitored to be complete by TLC analysis, the catalyst was removed by filtration, washed with ethanol (3 × 3 mL), and dried under vacuum for the next run. The organic fractions were then concentrated on a rotary evaporator to afford the desired biaryl in excellent yield. The crude products were further purified by recrystallization.

## 5. NMR spectra of the materials and products

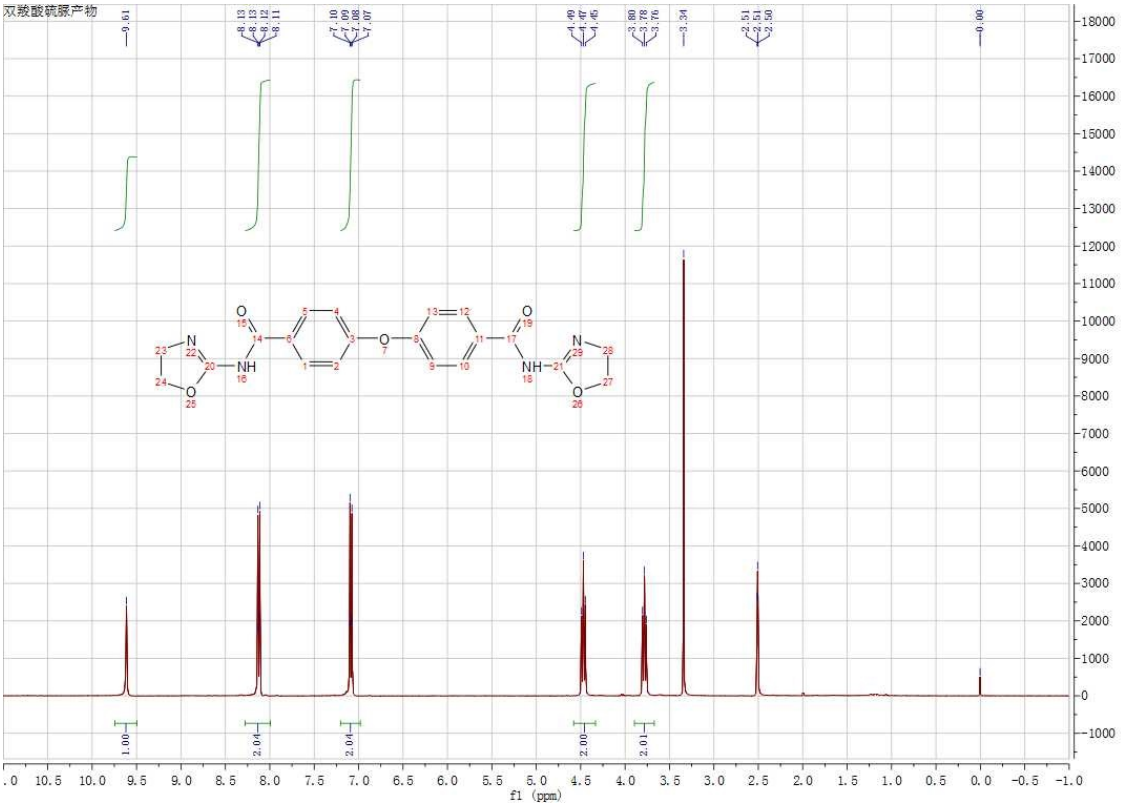
**$^{1}$H NMR of bisacylthiourea B**



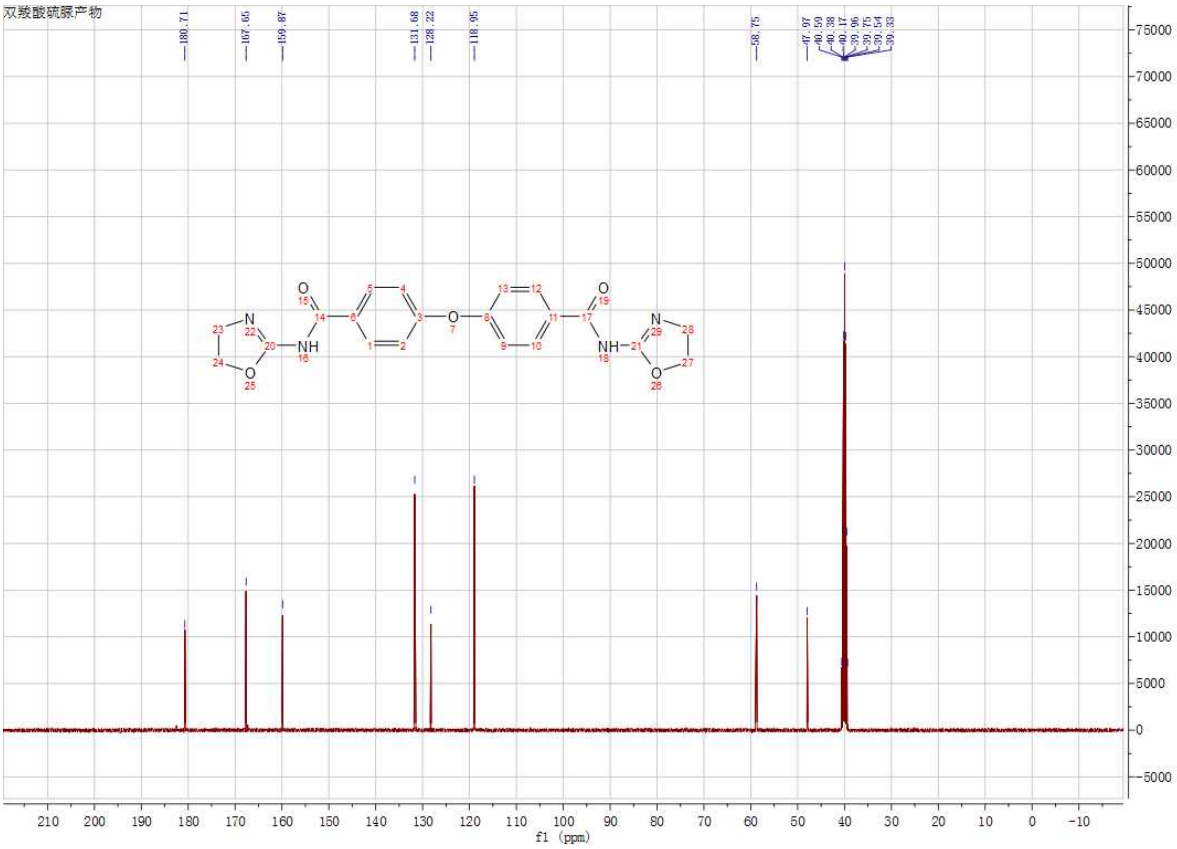

**$^{13}$C NMR of bisacylthiourea B**



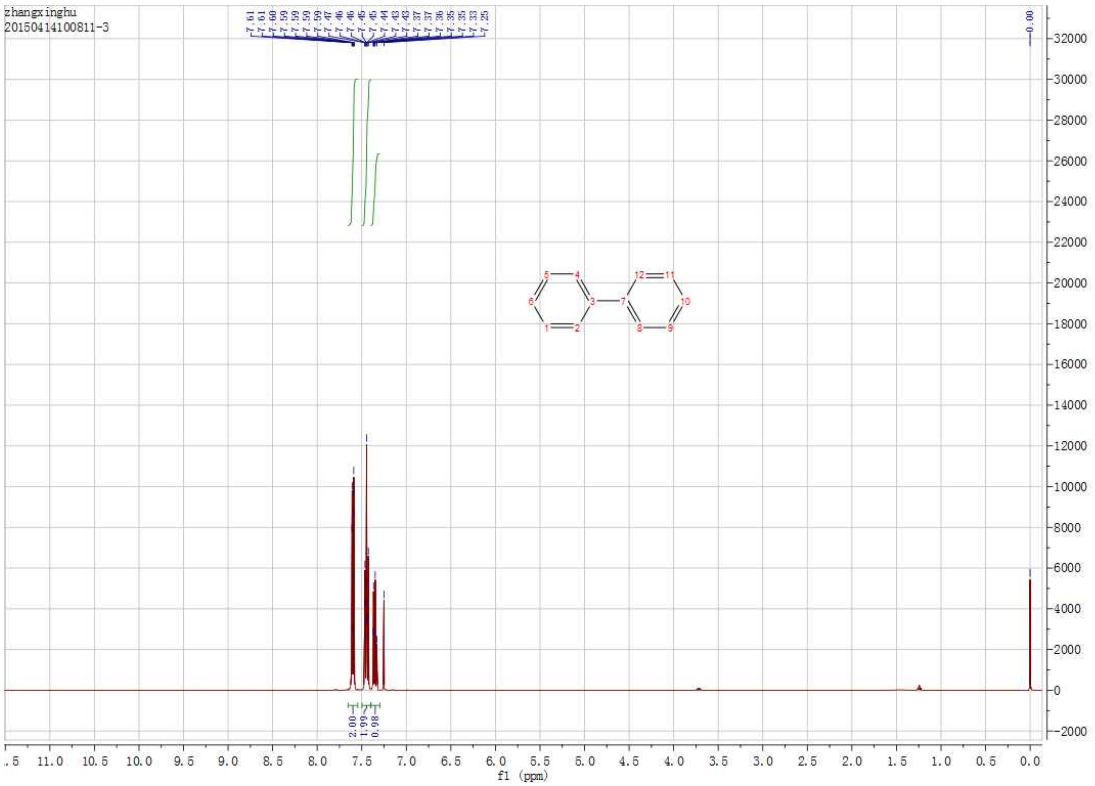

**$^{1}$H NMR of bisoxazoline C**



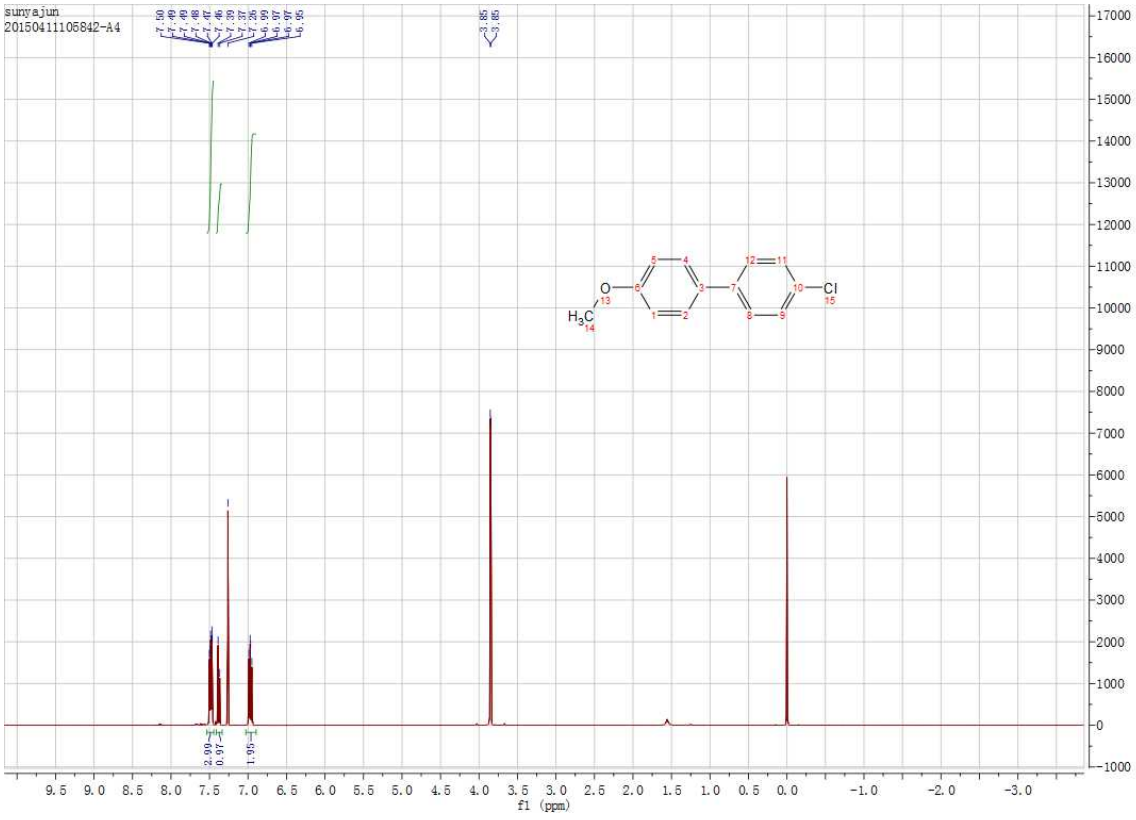

**$^{13}$C NMR of bisoxazoline C**

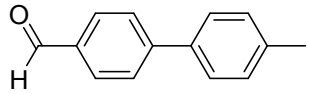



1. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 2H), 7.45 (ddd, $J$ = 7.8, 4.5, 1.2 Hz, 2H), 7.36 (dt, $J$ = 9.3, 4.3 Hz, 1H).

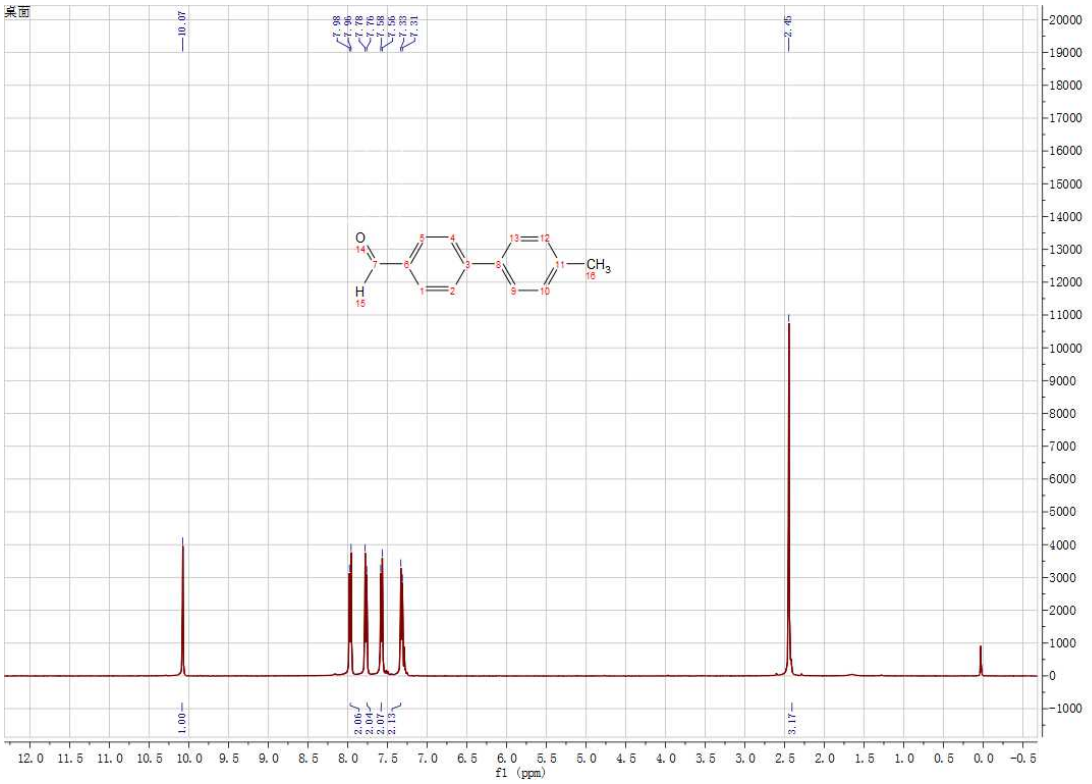


2. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 3H), 7.38 (d, *J* = 8.7 Hz, 1H), 6.97 (dd, *J* = 8.8, 6.5 Hz, 2H), 3.85 (d, *J* = 3.0 Hz, 3H).




3. 

$^1$H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.31 (s, 2H), 2.42 (s, 3H).

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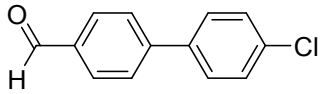
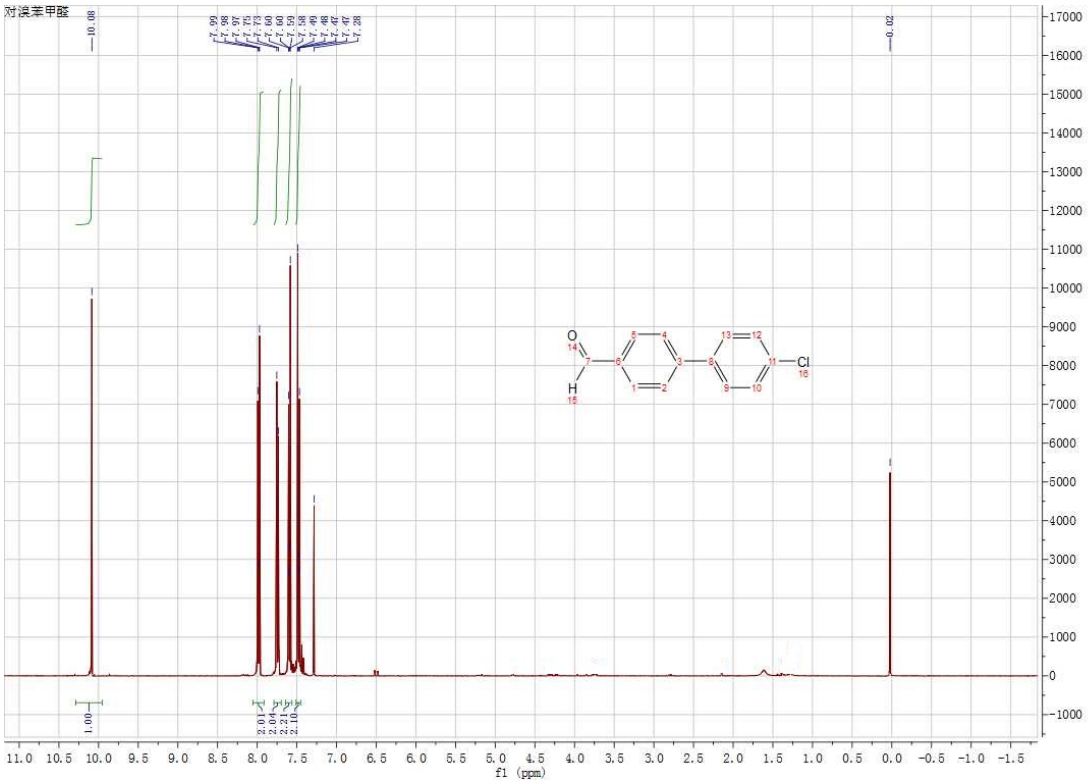



$^1$H NMR (400 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 3.92 – 1.13 (m, 1H).



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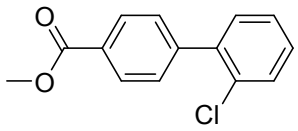
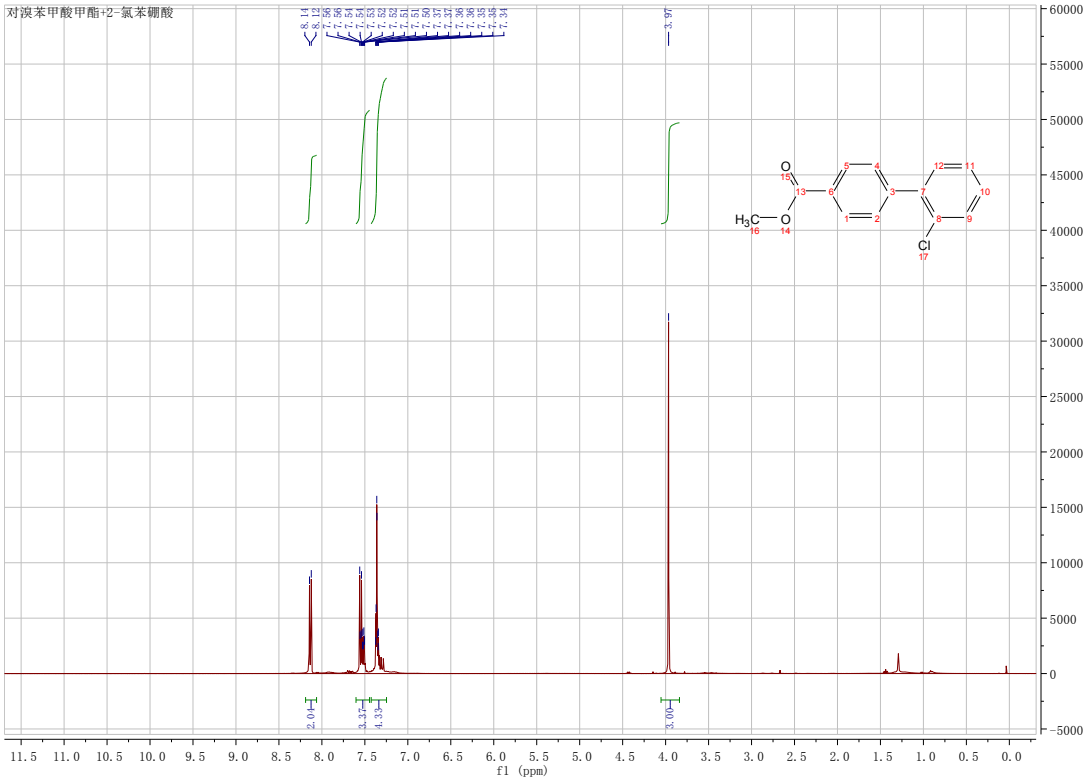


$^1$H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, $J$ = 8.2 Hz, 2H), 7.60 – 7.45 (m, 3H), 7.43 – 7.25 (m, 4H), 3.97 (s, 3H).

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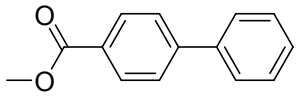
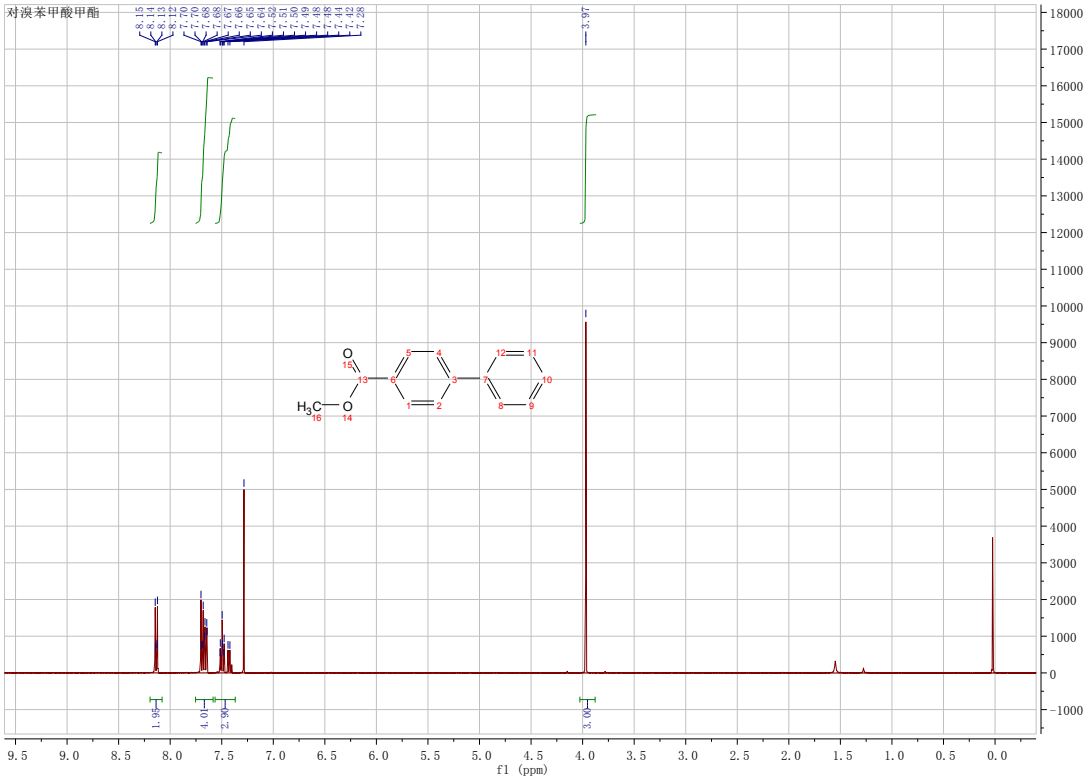


$^1$H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.08 (m, 2H), 7.67 (ddd, $J$ = 9.6, 7.4, 1.6 Hz, 4H), 7.48 (ddd, $J$ = 23.8, 15.2, 4.2 Hz, 3H), 3.97 (s, 3H).

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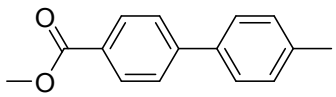
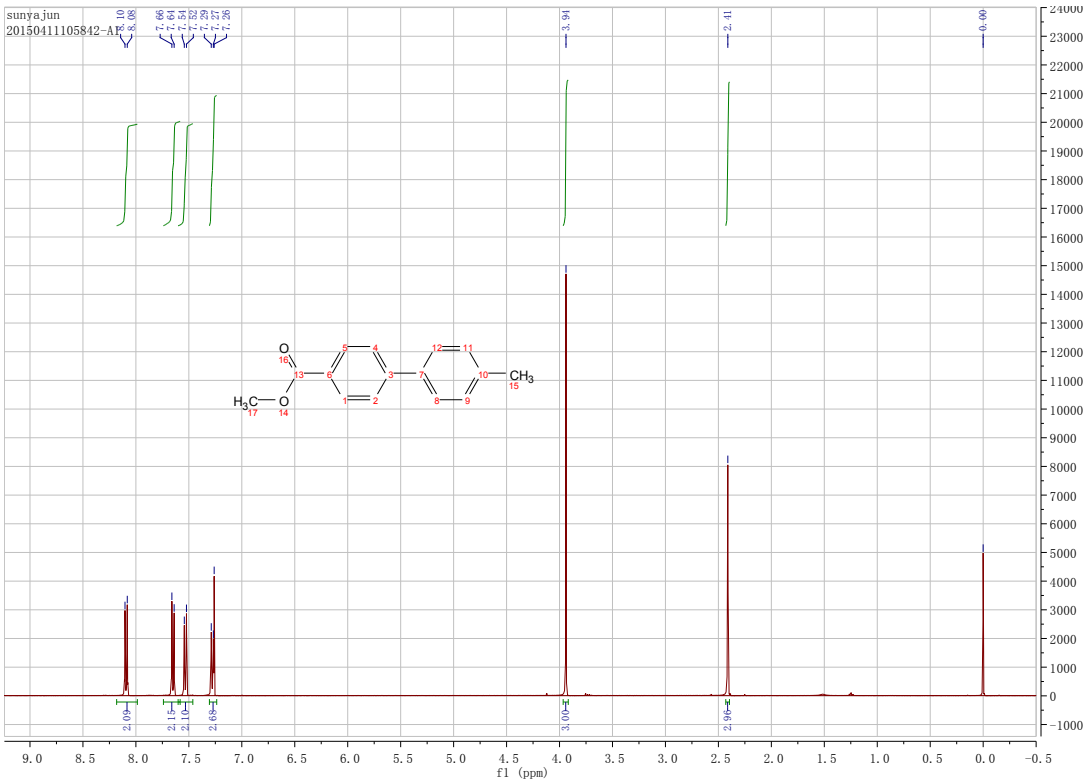


$^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, $J$ = 8.6 Hz, 2H), 7.65 (d, $J$ = 8.6 Hz, 2H), 7.53 (d, $J$ = 8.2 Hz, 2H), 7.31 – 7.24 (m, 3H), 3.94 (s, 3H), 2.41 (s, 3H).



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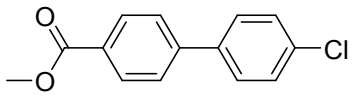
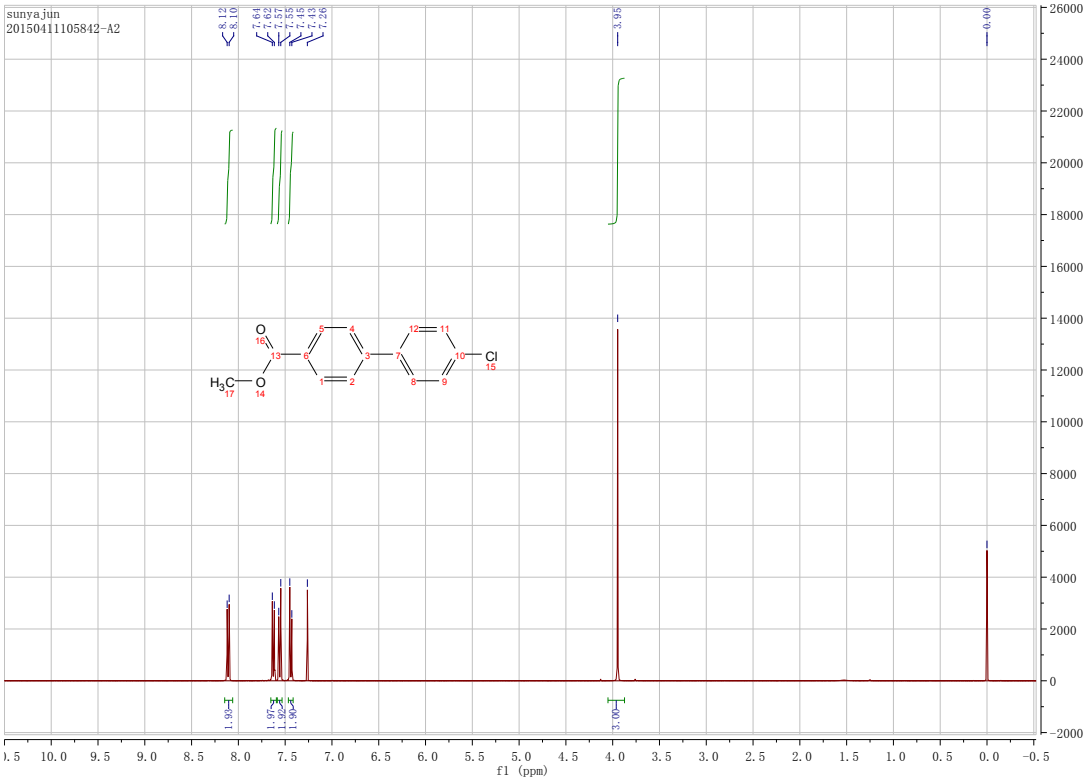
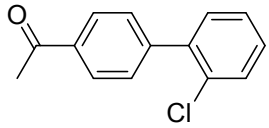


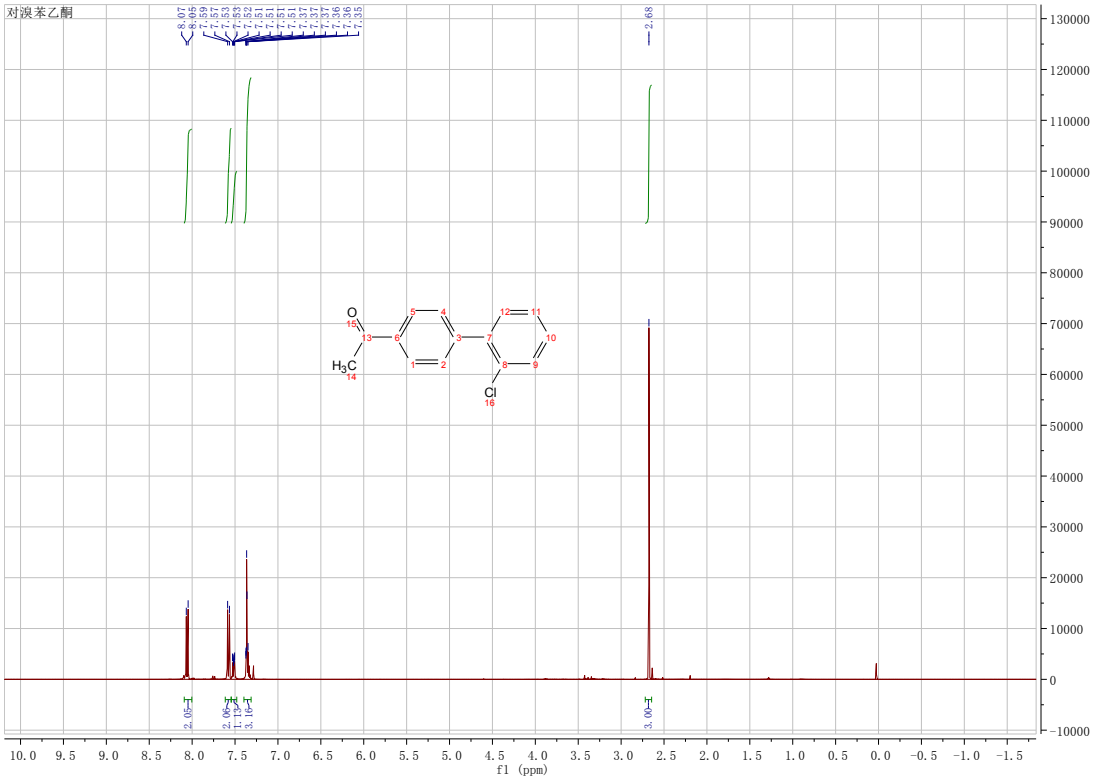

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 3.95 (s, 3H).




9.

$^1$H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.40 – 7.31 (m, 3H), 2.68 (s, 3H).

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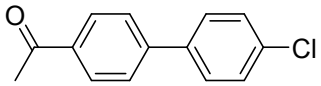
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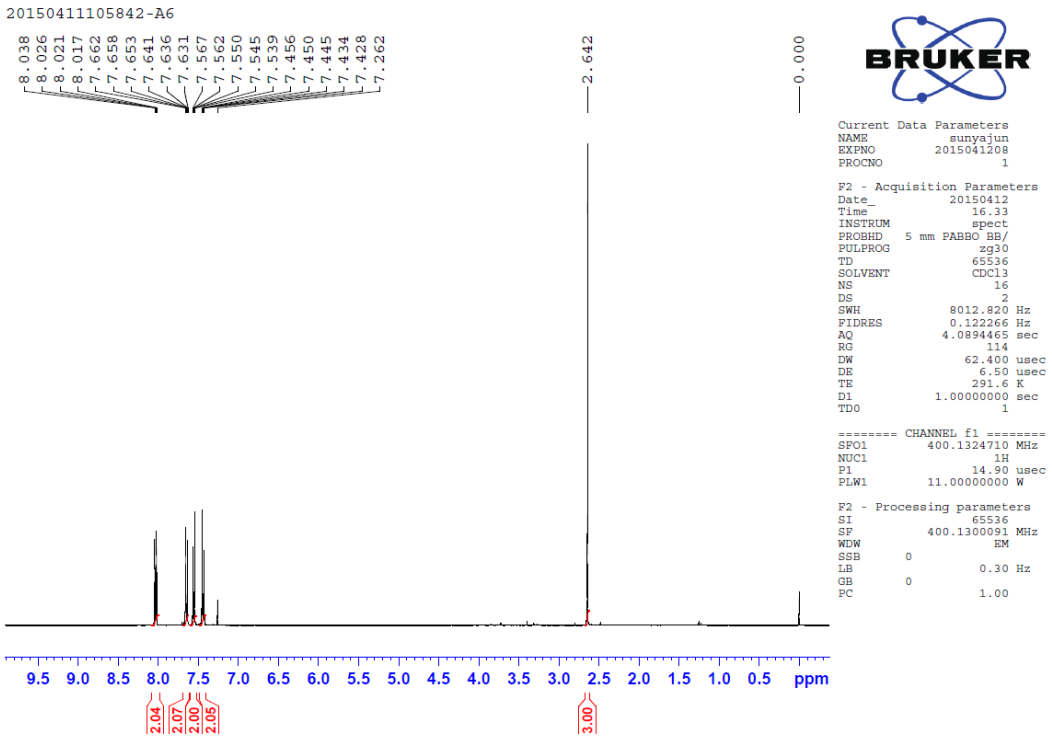
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